

國立中山大學八十八學年度碩博士班招生考試試題

科目：綜合化學 (化學系碩士班)

共 4 頁 第 1 頁

1. For a particle in a one-dimensional box, the Schrödinger equation is

$$-\frac{h^2}{8\pi^2m} \frac{d^2\psi}{dx^2} = E\psi \text{ inside the box } (0 \leq x \leq a) \text{ and the wall cannot be}$$

penetrated by the particle.

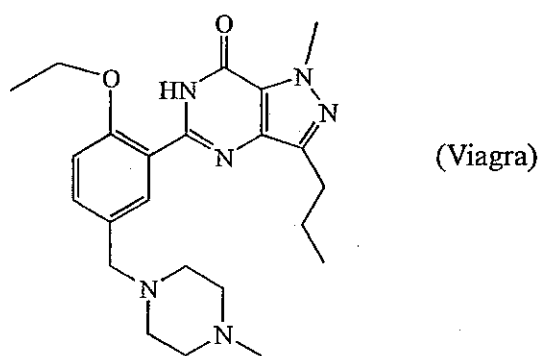
- Derive the normalized wave function ψ of this system. (5 points)
- Derive the energy expression of this system. (5 points)
- If the particle is in the ground state and the box is expanded adiabatically from the length a to $2a$, will the system make transitions to other states? Calculate the ΔE of this process. (5 points)
- If the particle is in the ground state and the box is expanded suddenly from the length a to $2a$, will the system make transitions to other states? Calculate the ΔE of this process. (5 points)

2. In the industrial syntheses of NH_3 from N_2 and H_2 , the operational conditions of the reactor are usually maintained at 300 atm and 500 °C. In the absence of Fe catalysts, the yield of NH_3 is too low to be economical. On the other hand, many bacteria and algae can fix nitrogen from the air with the help from an enzyme called nitrogenase in the earth environment. What is your comment on the roles of thermodynamic equilibria, reaction rates, and reaction mechanisms in the strategic planning of synthetic routes? (10 points)

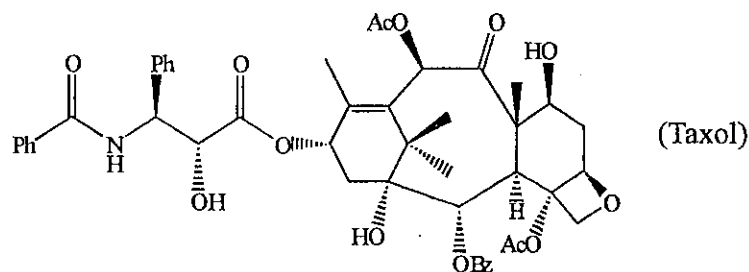
3. Plot out schematically the rotational population distributions of HCl gases at 300 K and 500 K. (5 points)

4. State the Arrhenius equation in chemical kinetics and define each term. (5 points)

5. The structural formula of viagra (a drug to treat impotence) is depicted below. Can you tell the reason why those pills are blue-colored? (5 points)

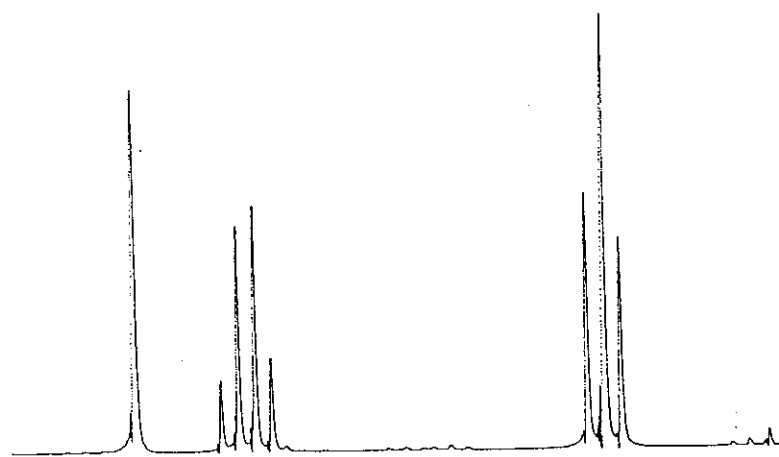


6. The structural formula of taxol (a drug to treat breast cancer) is depicted below. How many optical isomers this molecule can have? (5 points)

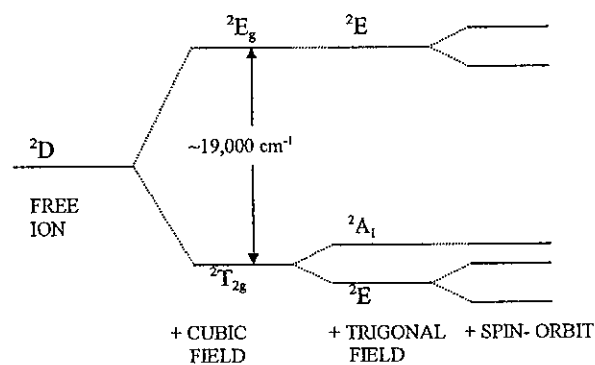


7. The future of the supply of raw chemicals relies on a) coal, b) crude oil, or c) biomass. Make a choice and defend your opinion scientifically. (10 points)

8. The $^1\text{H-NMR}$ spectrum of ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$) in CDCl_3 solvent is shown below. Identify the characteristic NMR peaks of the three groups of protons in the ethanol. Elaborate the physical reasons of their shifts and splittings. (10 points)

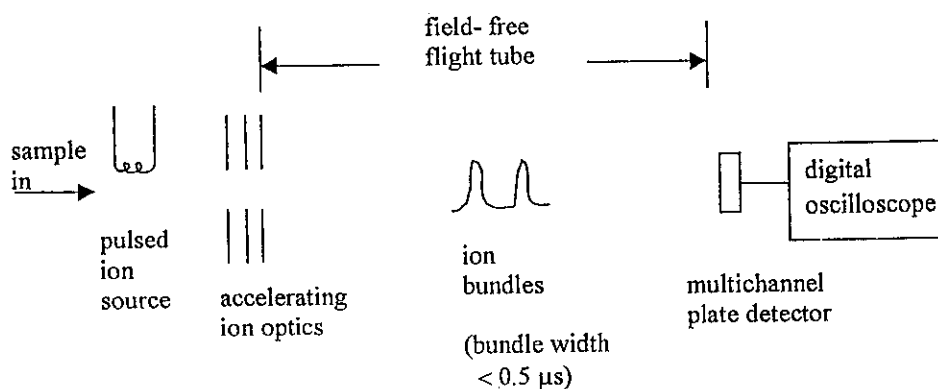


9. $\text{Ti}^{3+}/\text{Al}_2\text{O}_3$ (Ti: Sapphire) is a popular solid state laser crystal in recent years. The electronic configuration of Ti^{3+} is $[\text{Ar}]3d$. An energy level diagram of this system is depicted below. Discuss the meaning of the term symbols and their splittings under various interactions. What is the degeneracy of each energy level of a real $\text{Ti}^{3+}/\text{Al}_2\text{O}_3$ crystal? (10 points)



10. Have you ever utilized any chromatography apparatus in a chemical laboratory? Discuss their principles of separation. (10 points)

11. A schematic diagram of a time-of-flight (TOF) mass spectrometer is depicted below. The digital oscilloscope in this set up can differentiate two electric pulses separated by $1 \mu\text{s}$ easily. The researcher in charge of the TOF mass spectrometer tells us that his machine can resolve $^{12}\text{C}^{16}\text{O}^+$ (27.9949 amu) species from the $^{14}\text{N}_2^+$ (28.0060 amu) peak. If those ions have been accelerated to 2 keV (3.2×10^{-9} erg), what is the minimum length of the flight tube? (1 erg = $1 \text{ g}\cdot\text{cm}^2/\text{s}^2$) (10 points)



國立中山大學八十八學年度碩博士班招生考試試題

科目：物理化學與分析化學(化學系碩士班)

共 2 頁 第 / 頁

壹. 分析化學部分共 4 題 50 分

1. (10%) Define any two terms of the following list.

(Note: not "translation" of the terms from English to Chinese.)

null hypothesis	indeterminate errors	standard reference material
internal standard	differentiating solvents	auxiliary oxidizing reagents
buffer capacity	blank solutions	homogeneous precipitation
standardization	confidence level	EDTA displacement titration
relative supersaturation	electrical double layer of a colloid	

2. (10%) Describe (1) the principles (or mechanism) of any one of the following devices, and (2) the purpose of using that device.

(You may use a drawing to illustrate your description, but a drawing without explanation will not earn any credit.)

PMT	charge-coupled device (CCD)
interference filters	Echelle grating monochromators
Michelson interferometer	electrothermal atomizers
potentiostat	time-of-flight mass analyzers

3. (20%) Choose one set of the following instruments.

- (1) Briefly describe the advantages (or unique properties) of the underlined one over the others in the same set, and
- (2) describe the reason (principles or mechanism) why the underlined one has such unique properties.
 - (a) ICPMS, glow-discharge mass spectrometry, spark source mass spectrometry
 - (b) MALDI/MS, ES/MS, FAB/MS
 - (c) AFM, STM, SEM, TEM
 - (d) ESCA, Auger electron microscopy
 - (e) square-wave voltammetry, cyclic voltammetry, linear-scan voltammetry
 - (f) capillary electrophoresis, liquid chromatography, HPLC

4. (10%) Write down the correct procedures of

preparation of a pH 9.3 buffer solution.

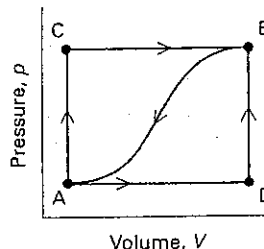
(You need to describe every preparation step and your calculation in detail.)

(note: NH_3 , $K_a 2.2 \times 10^{-5}$; CH_3COOH , $K_a 1.75 \times 10^{-5}$)

貳. 物理化學部分共 5 題 50 分

Physical Chemistry:

5. (12 points) When a system is taken from state A to state B along the path ACB in the Figure below, 80 J of heat flows into the system and the system does 30 J of work. (a) How much heat flows into the system along path ADB if the work done is 10 J? (b) When the system is returned from state B to A along the curved path, the work done on the system is 20 J. Does the system absorb or liberate heat, and how much? (c) if $U_D - U_A = +40$ J (U indicates internal energy), find the heat absorbed in the processes AD and DB.



6. (12 points) For three dimensions the metal can be treated as a rectangular box $A \times B \times C$. The appropriate wave function is the product of three sine or cosine functions and the energy is given by $E = h^2(n_A^2/A^2 + n_B^2/B^2 + n_C^2/C^2) / 8M_e$, where h is Planck constant and M_e is the electron mass. Suppose $(n_A^2/A^2 + n_B^2/B^2 + n_C^2/C^2) = 108$, (a) what is the value of degeneracy at this particular energy? (b) what are the degenerate states in terms their quantum numbers?
7. (8 points) Identify which of the following functions are eigenfunctions of both the operators d/dx and d^2/dx^2 ? Give their corresponding eigenvalues. (a) e^{ikx} (b) $\cos kx$ (c) k (d) kx (e) e^{-ax^2} .
8. (12 points) From the Maxwell distribution of molecular speeds $F(V)$, define what (a) the most probable speed, V_{mp} (b) the average speed, V_{av} (c) the root-mean-square speed, V^{rms} . At the same temperature, which speed is the largest among these three?
9. (6 points) Explain what the Arrhenius plot is. What information can you achieve in such a plot?

有機化學部分共 50 分, 4 大題

I. Choose the best answer and ONE answer only. (30 pts.)

1. The strongest acid is
(a) *p*-nitrobenzoic acid (b) *p*-bromobenzoic acid (c) *p*-methylbenzoic acid
(d) *p*-methoxybenzoic acid

2. Which of the following compounds is a bridged bicyclic alkane?

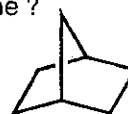
(a)



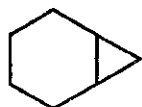
(b)



(c)



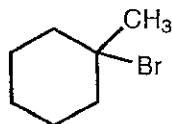
(d)



3. Which of the following compounds is a tertiary halide?

- (a) $(\text{CH}_3)_3\text{CCH}_2\text{Br}$ (b) $\text{CH}_3\text{CH}_2\text{Br}$ (c) $\text{CH}_3\text{CH}=\text{CHBr}$

(d)



4. Which of the following alkenes is most stable?

- (a) cyclobutene (b) *trans*-2-pentene (c) *cis*-2-pentene (d) 1-pentene

5. Which of the following alkyl halides would be suitable for formation of a Grignard reagent?

- (a) $\text{H}_2\text{NCH}_2\text{CH}_2\text{Br}$ (b) $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{Br}$ (c) $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{Br}$
(d) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CN}$

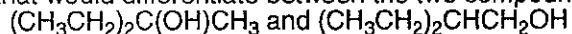
6. Which of the following groups most strongly activates an aromatic ring for nucleophilic substitution?

- (a) $-\text{OH}$ (b) $-\text{NO}_2$ (c) $-\text{CHO}$ (d) $-\text{CH}_3$

7. The kind of spectroscopy which is best for determining the functional groups in a molecule is

- (a) UV (b) MS (c) IR (d) NMR

8. The test that would differentiate between the two compounds below:



- (a) Tollen's test (b) Baeyer test (c) Sodium fusion test (d) Lucas test

9. The conversion of 2-butanone to propanoic acid is best accomplished with

- (a) 1. ozone; 2. H_2O_2 (b) NaOH , I_2 (c) Ag_2O , Br_2 (d) LiAlH_4

10. The ylide

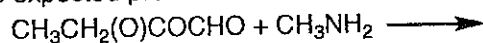
- (a) Ph_3P (b) $\text{Ph}_3\text{P}^+\text{CH}_3\text{Br}^-$ (c) $\text{Ph}_3\text{P}^+\text{CH}_2^-$ (d) $\text{C}^-\text{H}(\text{CO}_2\text{Et})_2$

有機化學部分

11. The class of compounds which would be expected to show IR absorption around 2200 cm^{-1}

- (a) CH_3CN (b) acid chlorides (c) $\text{CH}_3\text{NH}(\text{O})\text{CCH}_3$ (d) $\text{CH}_3\text{C}(\text{O})\text{NH}_2$

12. The expected product of the reaction below.



- (a) CH_3NHCHO (b) CH_3CN (c) $\text{CH}_3\text{NH}(\text{O})\text{CCH}_2\text{CH}_3$ (d) $\text{CH}_3\text{C}(\text{O})\text{NH}_2$

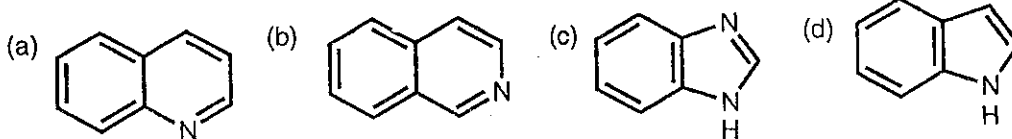
13. The type of natural product often found in perfumes.

- (a) phospholipids (b) steroids (c) prostaglandins (d) terpenes

14. Which of the following molecules would function as an initiator in free-radical polymerization.

- (a) $\text{Ph}(\text{O})\text{COOC}(\text{O})\text{Ph}$ (b) $\text{CH}_3\text{CH}(\text{OCH}_3)_2$ (c) PhCO_2H (d) PhOH

15. Which of the following compounds is indole?

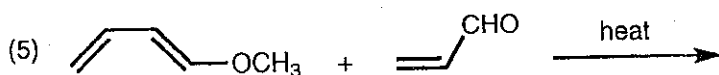
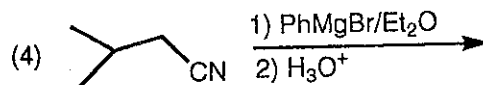
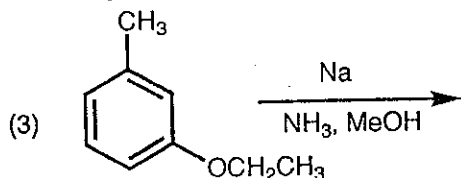
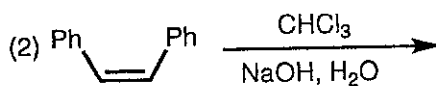
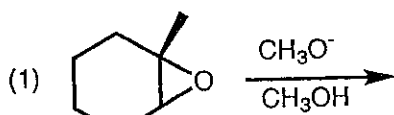


II. Give structure for the following compounds (6 pts.)

- (1) benzyl alcohol (2) 2-furylmethyl benzoate
 (3) *trans*-3-chloro-1,2-epoxycyclohexane

III. The ^{13}C NMR spectrum of compound A shows only 4 peaks. If A has a molecular formula $\text{C}_5\text{H}_9\text{Br}$, draw a structure for A that fits these data. (4 pts.)

IV. Write structure for the products of the following reactions. (Include stereochemistry where appropriate) (10 pts.)



國立中山大學八十八學年度碩博士班招生考試試題

科目：有機化學與無機化學

共 4 頁 第 3 頁

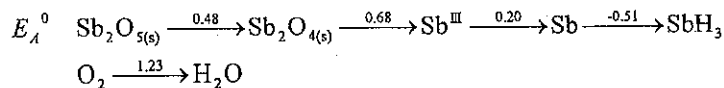
無機化學部分，共 50 分 三大題

一、True or false.(14pts)

1. Glacial acetic acid may dissolve in H₂O and benzene.
2. Deep-sea divers breathe a mixture of He and O₂ instead of air to get rid of the caisson disease.
3. The Xe-F bonds of XeF₂ have a bond order of 0.5.
4. Iodine molecule has the highest boiling point among the I₂, H₂O, diethyl ether, and ethylene.
5. RuO₄ is an ionic compound.
6. The Ti⁴⁺ is harder than Pb⁴⁺.
7. Dissolving FeCl₃ into water will turn the litmus paper to red.

二、Choose the right answer.(16pts)

1. Which one shows the lowest frequency of CO stretching in the IR spectrum? (1)Ni(CO)₄ (2)[Co(CO)₄]⁻ (3)[Fe(CO)₄]²⁻ (4)[Mn(CO)₅]¹⁻ (5)Fe(CO)₅.
2. Given the following emf diagram of antimony in acidic solution:



Which one is unstable in acidic solution? (1)Sb₂O₅ (2)Sb₂O₄ (3)Sb^{III} (4)Sb (5)SbH₃.

3. Which of the following is not a d-block element? (1)Y (2)Tc (3)Zr (4)Tl (5)Ta
4. Which of the following is the electron-rich compound? (1)CH₄ (2)B₂H₆ (3)Al₂(C₂H₅)₄H₂ (4)NH₃ (5)[BH₄]⁻
5. Which one is the conductive metallic hydride? (1)PdH_{0.9} (2)CaH₂ (3)AsH₃ (4)SiH₄ (5)NaH
6. Which one can react most easily with alkylhalide via free radical process? (1) (CH₃)₃SnH (2) (CH₃)₃SiH (3)NH₃ (4)H₂O (5)C₂H₆
7. The intermediate [Fe(SCN)(OH₂)₅]²⁺ can be obtained in the reaction of [Co(NCS)(NH₃)₅]²⁺ with Fe²⁺_(aq). Therefore, we can predict that (1) the reaction mechanism is I_d, (2) the reaction mechanism is D, (3) the reaction mechanism is outer sphere electron transfer, (4) the reaction mechanism is inner sphere electron transfer, (5) the product of this reaction is [Fe(SCN)(OH₂)₅]³⁺.
8. The most stable term of a lithium(+) cation is (1)¹S (2)²D (3)⁰S (4)²S (5)³P

三、Answer the following problems.

1. Draw a 2p_x and a 3p_z atomic orbital contours on the same coordinate system.(3pts)
2. Draw the molecular structure of the following ligands: 1,10-phenanthroline and η³-allyl.(2pts)

國立中山大學八十八學年度碩博士班招生考試試題

科目：有機化學與無機化學

共 4 頁 第 4 頁

3. Draw the molecular structure of (1)Pentaammine(nitrito-O)cobalt(III) sulfate (2) Λ -[Co(en)₃]³⁺ (3) Tri- μ -carbonyl bis(tricarbonyliron).(3pts)
4. On the same energy scale draw the d orbital energy levels of (1)a free ion (2)an ion in a spherical symmetric field (3)an ion in an octahedral complex.(3pts)
5. Finish the chemical equation of " $2\text{RhCl}_3 + 4\text{CO} \rightarrow$ " and draw the molecular structure of the Rh product. (3pts)
6. Describe what you will observe if, with no stirring, 0.2g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is added into 5mL water and followed by adding 1mL concentrated ammonia aqueous solution.(6pts)